

AN EXPERIMENTAL STUDY OF HYDRATE CRYSTAL GROWTH FROM METHANE, CARBON DIOXIDE, AND METHANE+PROPANE MIXTURES

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Introduction and Background

Gas hydrates are crystalline inclusion compounds composed of water and natural gas in non-stoichiometric ratios varying from 5.67 to 17 water molecules per hydrated gas molecule (Holder, Zetts and Pradham, 1988; Sloan, 1990). Hydrate crystals represent one of the few phases and perhaps the only condensed phase where water and light non-polar gases exist together in significant proportions and are of particular interest to the petroleum and natural gas industries because of their potential as a separating agent, their potential as a storage vehicle and their undesired ability to plug gas transportation lines (Holder and Enick, 1995).

Gas-water mixtures will form crystals which coat the walls of and potentially plug gas transportation lines causing the cessation of gas or gas+oil flow (Lingelem, Majeed and Stange, 1994). When producing oil or gas, one goal of industry is to understand the conditions under which operation is possible without plugging. One such operating condition is where the hydrates are thermodynamically unstable. Such conditions are generally present when operating at temperatures above 25 C, although the temperature depends upon pressure, usually 50-200 Mpa, and gas composition, usually 95+% methane. Sufficiently high temperatures are generally not present when producing gas in offshore operations, because deep ocean waters are seldom warmer than 4-8 C. To prevent hydrate formation operators will generally inject methanol which acts as an antifreeze and destabilizes hydrates. Effective methanol concentrations are generally 10-50%, by weight, of the water+methanol liquid.

Sometimes, it is not desirable or possible to operate at conditions where hydrates are thermodynamically unstable. Such conditions may occur if methanol injection facilities fail or in cases where methanol injection and recovery are prohibitively expensive. In such cases it is desirable to understand for what duration, operation of a gas transportation line is possible without the complete plugging of the line by hydrates. To more completely understand this question, the rates at which hydrates form must be understood. The process includes the nucleation of hydrates on a heterogeneous surface, such as the pipewall, and the growth of these hydrates towards the center of the pipeline. This scenario for hydrate growth is deemed most likely for two reasons. First, the pipewall is generally the coldest part of the transportation line and hence the location where hydrates are most thermodynamically stable. Second, the formation of crystalline hydrates normally requires a solid nucleation site and the pipewall is generally the only source of such sites. Crystals can subsequently abraid from the pipewall and be transported down the pipeline, but such abraided crystals are not expected to be the primary cause of initial flow constriction.

In the present study, we determine the rates at which hydrates nucleate and grow on the surface of a cold pipewall over which gas is flowing at rates comparable to those which might exist in a pipeline.

Experimental

The apparatus for studying the precipitation and growth of solids is a variation of that described elsewhere (Figure 1 Holder and Enick, 1995). The apparatus consists of two coaxial cylinders. Hydrates form in the annular space by growing radially inward from the cooled outer wall. To form hydrates, the temperature controlled vessel is pressurized with the appropriate gas, 100-150 ml of water are injected and the inner cylinder rotated. The vessel can be operated in a vertical position as shown in Figure 1 or in a horizontal position. For these experiments a horizontal

position was used exclusively. The fundamental improvement of this apparatus relative to cells used in the past is that gas will flow in the annular space over the hydrate formation surface rather than remaining static. This will provide a means of investigating the effects of gas shear stress at the hydrate forming surface in pipelines.

Temperature gradients within this vessel are established by flowing methanol/water mixtures from separate isothermal baths through cooling coils on the outside of the vessel and the inner cooling chamber. The water in the vessel would coat the rotating inner cylinder, evaporate, and condense on the inside of the outer cylinder.

A temperature gradient was established across the annular gap. The surface of the water was then in direct contact with the flowing methane at 273K - 275K. Hydrates began to form inside the outer cylinder. Pressure decreased as the methane from the gas phase entered the hydrate phase and was used to deliver the amount of water converted to hydrate.

Experiments continued until either 1) the pressure of the methane remained constant, indicating that hydrate formation had ceased or 2) the rotation of the inner cylinder ceased because small amounts of hydrates clogged the bearings and friction surfaces. The system was then depressurized and the hydrate crystals examined before they had an opportunity to completely dissociate. The hydrates formed a relatively uniform layer of frost-like solid in the annular gap.

Results

We have measured the linear growth rate of hydrates formed from pure methane, pure carbon dioxide, two mixtures of methane+propane whose compositions were (95% methane and 5% propane) and (97% methane and 3% propane). The important variables in these studies were gas flow rate, gas composition, temperature, and pressure. Table 1 lists the results.

Gas flow rate: Higher gas flow rates (reported as RPM) tend to produce higher rates of hydrate formation. This is because the higher gas flow rates dissipate the considerable heat release generated during hydrate formation (50-100 kJ per mole of hydrated gas) and because the higher gas flow rates improve the mass transfer of water to the hydrate forming surface. It is still not clear which of these factors is most significant. However, the effect of gas flow rate appears to level off at the highest rates. This means that mass and heat transfer are no longer limiting and a true kinetic value for hydrate growth is obtained. The higher gas flow rates used here are comparable to pipeline Reynolds numbers in excess of 10,000 and thus these conditions are those that might be obtained in an actual gas pipeline.

Gas composition: It was observed that no clear difference in growth rates for the 95% methane and 97% methane mixtures were observed, but rates for gas mixtures and for carbon dioxide were faster than for pure methane. The methane hydrate is the least thermodynamically stable and it appears that the thermodynamic driving force (difference between the equilibrium temperature and the actual experimental temperature at the hydrate surface) affects the rate at which hydrates form. Another factor which may be important is the ability to stabilize the large cavity of the hydrate structure. Propane stabilizes the large cavity of structure II better than methane and carbon dioxide stabilizes the large cavity of structure I better than methane. The ability to stabilize the large cavity may play a role in the kinetics. The current experimental evidence is not conclusive on this issue.

Another variable of interest for the methane+propane mixtures is that the gas composition changes as the hydrates form since the propane concentration in the hydrates is much higher than in the gas phase. As more hydrates form a eutectic mixture of methane and propane containing less than 1% propane should be present. This mixture should result in the simultaneous formation of both structure I and structure II hydrate.

Temperature: In general, temperature is thought to increase the rate of any kinetic process. However, higher gas temperatures decrease the thermodynamic driving force and will tend to impede the rate.

Pressure: The range of pressures used was small, but the results indicate that higher pressures increased the rate of hydrate formation.

Inhibitors: Both WAX and PVP reduced the rate of hydrate formation to negligible values when present. Both were applied to the inside surface of the outer cylinder prior to hydrate formation.

The overall correlation for growth rate for both methane + propane mixture is

$$\text{linear rate} = 0.001535 (\text{RPM}) + 9.3 \times 10^{-6} (\text{P/KPA}) \\ - 0.0178 (\text{Cooling Coil (T/K)}).$$

This correlation has a R^2 of 0.75.

Conclusion

The rates of hydrate formation along pipe walls will likely be comparable to the rates measured in this study. Linear growth rates of 0.2 cm/hr are likely to represent the maximum growth rate that could be expected in gas transportation lines. As the hydrates thicken, they can serve as insulators of the line which will result in slower cooling of the produced fluids (which come out of the earth at higher temperatures than exist in the transportation line). The insulation will produce higher transportation temperatures and could either enhance or inhibit hydrate formation rates.

Based upon the rates measured here, transportation lines could be operated for hundreds or thousands of hours prior to their blockage by hydrates.

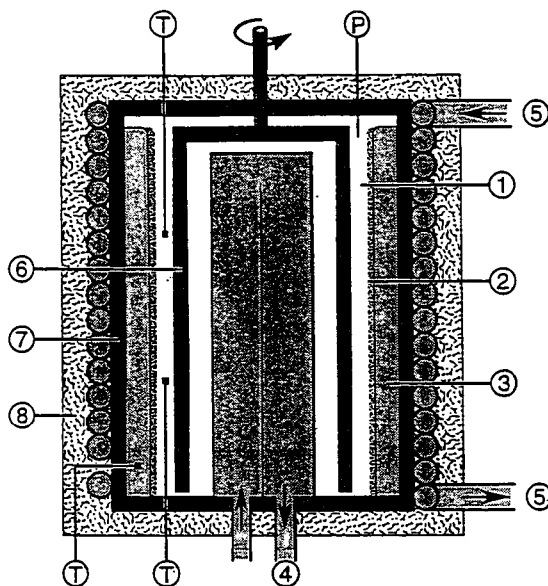
Acknowledgment

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Figure 1. High Pressure Tangential Annular Flow Apparatus



1. High Pressure Gas
 2. Gas Hydrate
 - 3.
 4. Gas Cooling Fluid Flowing in Cylinder
 5. Ice Cooling Fluid Flowing in Coils
 6. Rotating Cylinder
 7. High Pressure Cell
 8. Insulation
- T - Thermocouples
P - Pressure Transducer

Table 1: Growth Rate of Hydrates

Gas Composition	Bulk gas Temp (K)	Cooling coil Temp (K)	Initial Press (KPa)	RPM	Linear growth rate (cm/hr)
100% C ₁	283.7 +/- 0.4	273.7 +/- 0.3	6509	7	0.02
100% C ₁	283.5 +/- 0.5	271.4 +/- 0.1	6039	8	0.02
100% C ₁	282.9 +/- 0.4	272.0 +/- 0.3	6021	8	0.05
100% C ₁	282.1 +/- 0.4	271.9 +/- 0.1	6023	8	0.00
100% C ₁	281.9 +/- 0.3	272.1 +/- 0.1	5987	30	0.02
100% C ₁	283.0 +/- 0.5	271.8 +/- 0.1	6004	2	0.01
100% C ₁	282.3 +/- 0.7	271.9 +/- 0.2	6019	8	0.02
100% C ₁	279.7 +/- 0.6	271.5 +/- 0.2	6861	25	0.02
100% C ₁	276.5 +/- 0.2	271.5 +/- 0.2	6618	15	0.02
5% C ₂ :95% C ₁	291.1 +/- 0.3	272.9 +/- 0.1	7014	7	0.08
5% C ₂ :95% C ₁	288.9 +/- 0.4	273.6 +/- 0.2	7110	15	0.11
5% C ₂ :95% C ₁	288.7 +/- 0.6	270 +/- 0.1	6905	60	0.15
5% C ₂ :95% C ₁	288.4 +/- 0.7	271.1 +/- 0.1	6940	1	0.03
5% C ₂ :95% C ₁	287 +/- 0.9	270 +/- 0.1	7089	30	0.17
3% C ₂ :97% C ₁	284.7 +/- 0.7	271.6 +/- 0.1	6781	7	0.03
3% C ₂ :97% C ₁	288.1 +/- 0.1	273.2 +/- 0.1	7036	7	0.05
3% C ₂ :97% C ₁	284.5 +/- 0.1	271.7 +/- 0.1	6782	60	0.15
3% C ₂ :97% C ₁	286.8 +/- 0.2	274 +/- 0.1	7016	2	0.08
3% C ₂ :97% C ₁	287.5	271.5 +/- 0.1	6927	2	0.13
3% C ₂ :95% C ₁	286.4 +/- 0.1	273 +/- 0.1	7011	30	0.06
CO ₂	282 +/- 0.3	271.4 +/- 0.1	3555	8	0.10
CH ₄ /WAX	277.8 +/- 0.7	271.6 +/- 0.2	5296	15	0.002
CH ₄ /PVP	278.6 +/- 0.6	272.1 +/- 0.2	5482	15	0.000